Efficient evaluation of quantum and thermal nuclear fluctuations in solids

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Self-consistent harmonic approximation

What is the SCHA?

The **S**elf-**C**onsistent **H**armonic **A**pproximation is a numerical tool to account for both thermal and **quantum** fluctuations of nuclei.

- Vibrational properties
  - Vibrational spectrum
  - Thermal conductivity (Ionic)
- Structural stability
  - First-order phase transitions
  - Second-order phase transitions

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How does the SCHA work?

- The free energy satisfies the Helmholtz least principle:

$$F = \min_{\rho} \left[U(\rho) - TS(\rho)\right] = \min_{\rho} \left[\left\langle H \right\rangle_{\rho} + k_b T \left\langle \ln \rho \right\rangle_{\rho}\right]$$

$\rho =$ Ionic density matrix

- the density matrix $\rho(\vec{R})$ is restricted to a multidimensional **Gaussian**:

$$\langle \vec{R} | \rho_S | \vec{R} \rangle = \sqrt{\frac{\det \Upsilon}{(2\pi)^D}} \exp\left[-\frac{1}{2} \sum_{ab}^{3N} (R_a - \mathcal{R}_a) \cdot \Upsilon_{ab} \cdot (R_b - \mathcal{R}_b)\right]$$

$\vec{\mathcal{R}}$ are the centroid positions Υ is the covariance matrix

- $\rho_S(\vec{R})$ is the solution of a **harmonic** Hamiltonian $\mathcal{H}$

$$\rho_S = \frac{\exp\left(-\mathcal{H}/k_b T\right)}{Z}$$

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Why should we use a Gaussian?

$$\rho_S = \textbf{Gaussian} = \rho_S(\vec{\mathcal{R}}, \boldsymbol{\Upsilon})$$

$$F = \min_{\vec{\mathcal{R}}, \boldsymbol{\Upsilon}} \left[U(\vec{\mathcal{R}}, \boldsymbol{\Upsilon}) - TS(\vec{\mathcal{R}}, \boldsymbol{\Upsilon}) \right]$$

Using a Gaussian *ansatz* for the density matrix have a lot of advantages:

- A limited number of degrees of freedom
  (if compared with other mean-field approaches)
- Both $S(\rho_S)$ and the kinetic part of $U(\rho_S)$ are known analytically.
- The potential energy can be efficiently evaluated by **Monte Carlo**.

Computationally cheap!

No thermodynamic integration required to evaluate the free energy.

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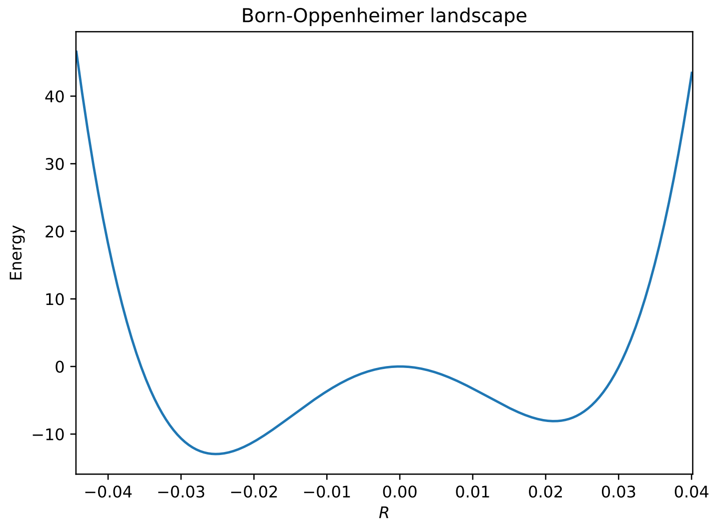
1D example at $T = 0$ K



1D example at $T = 0$ K

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2} + V(R)$$

- Exact energy:

$$E = \min_{\rho} \mathrm{Tr}[\rho H]$$

- Quasi-Harmonic (QHA) energy:

$$E_{QHA} = \min_{R} V(R) + \hbar\omega/2 \qquad \omega = \sqrt{\frac{1}{m}\left.\frac{d^2V}{dR^2}\right|_{R=R_{min}}}$$

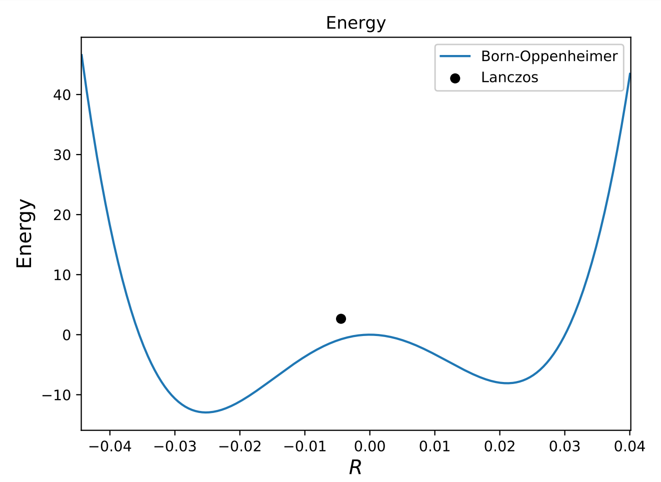
- SCHA energy:

$$E_{SCHA} = \min_{\mathcal{R},\Upsilon} \mathrm{Tr}[\rho_S H] \qquad \mathrm{Tr}[\rho_S H] = \frac{\hbar^2\Upsilon}{8m} + \left\langle V(R)\right\rangle_s$$

1D example at $T = 0$ K

Exact energy:

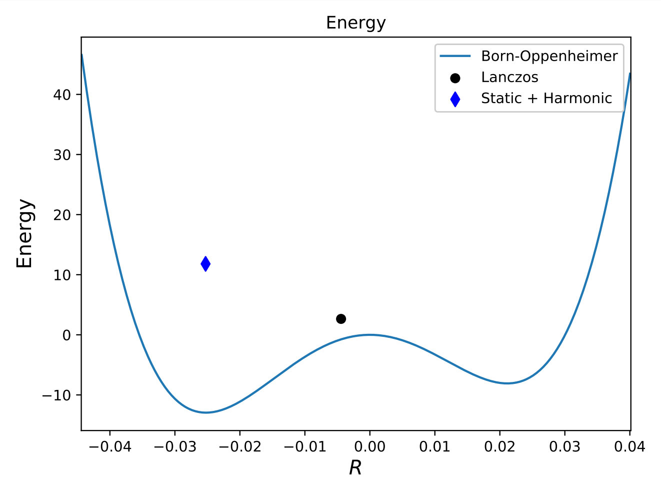
$$E = \min_{\rho} \mathrm{Tr}[\rho H]$$



1D example at $T = 0$ K

Harmonic energy:

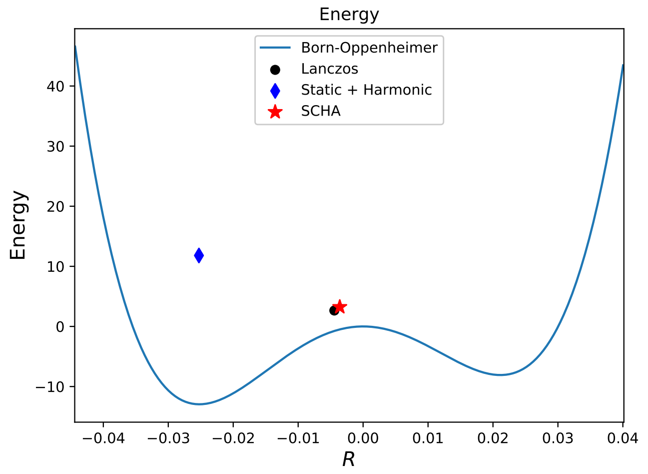
$$E_{QHA} = \min_R V(R) + \hbar\omega/2$$



1D example at $T = 0$ K

Scha energy:

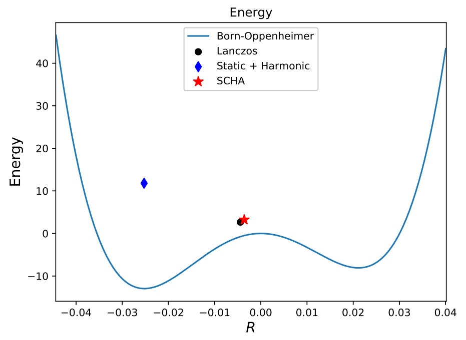
$$E_{SCHA} = \min_{\mathcal{R},\Upsilon} \mathrm{Tr}[\rho_S H]$$

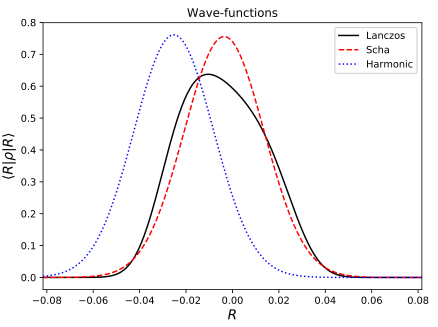


1D example at $T = 0$ K

👍 The **energy** and the **centroid position** are very good.

👎 The **wave-function** shape is not as good as the energy.





Structure relaxation

The standard relaxation

1. Initialize the atomic position.
2. Relax the atomic position.
3. Relax the unit cell.
4. Compute phonon dispersion.

The SCHA relaxation

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The SCHA relaxation

1) We initialize the SSCHA calculation with the density matrix that is the solution of the Harmonic Hamiltonian.

Structure relaxation

The standard relaxation

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The SCHA relaxation

2) We perform the minimization with respect to $\vec{\mathcal{R}}$ and $\boldsymbol{\Upsilon}$.

Structure relaxation

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The SCHA relaxation

3) We can compute the derivative of the free energy to get the stress tensor that includes the ionic contribution on quantum and thermal fluctuations:

$$P_{\alpha\beta} = -\frac{1}{\Omega}\frac{dF}{d\varepsilon_{\alpha\beta}}$$

$\Omega =$ Volume $\qquad$ $\varepsilon =$ Strain tensor

[1] Monacelli et. al. *Pressure and stress tensor of complex anharmonic crystals within the stochastic self-consistent harmonic approximation*, PRB 98, 2, 2018

Structure relaxation

The standard relaxation

1. Initialize the atomic position.
2. Relax the atomic position.
3. Relax the unit cell.
4. Compute phonon dispersion.

The SCHA relaxation

4) We can study the structure stability computing the second derivative of the free energy with respect to the atomic positions:

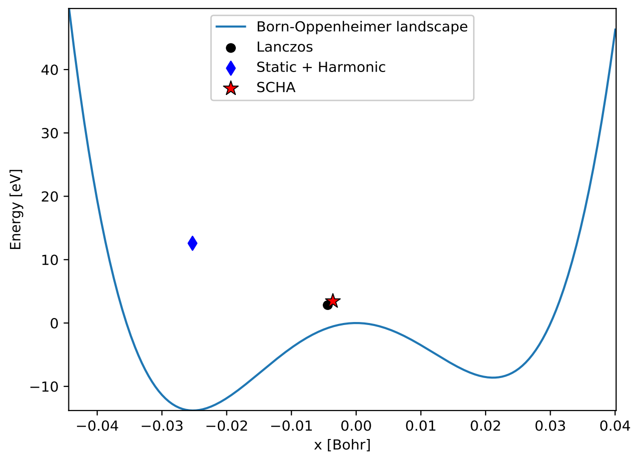
$$\frac{d^2 F}{d\mathcal{R}_a d\mathcal{R}_b}$$

[2] Bianco et. al. *Second-order structural phase transitions, free energy curvature, and temperature-dependent anharmonic phonons in the self-consistent harmonic approximation: Theory and stochastic implementation*, PRB 96, 014111, 2017

Structure stability

- Harmonic approx. has imaginary phonons
- We can define a SCHA energy landscape

$$E_s(\mathcal{R}) = \min_\Upsilon \mathrm{Tr}[\rho_S(\mathcal{R}, \Upsilon) H]$$



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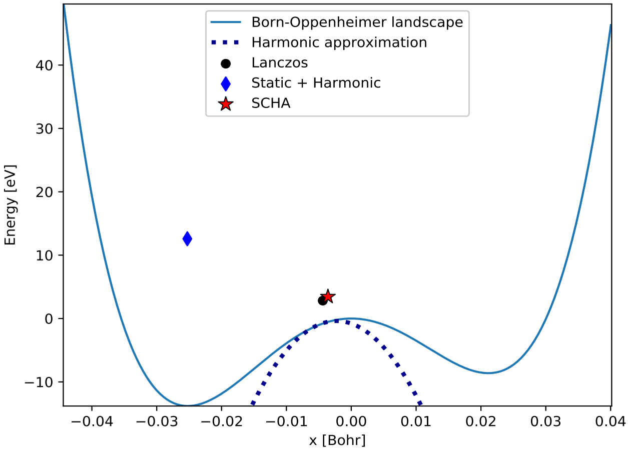

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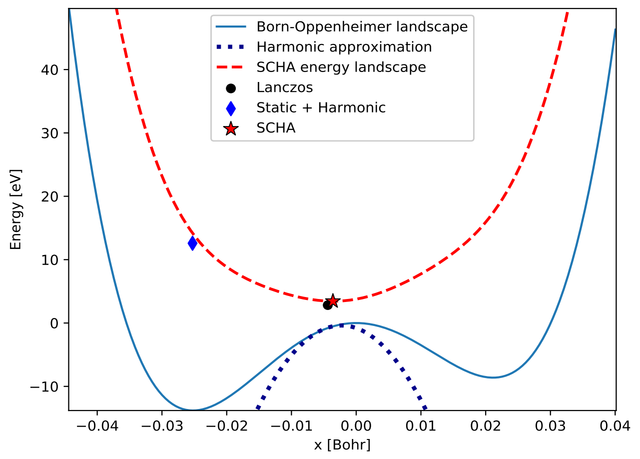
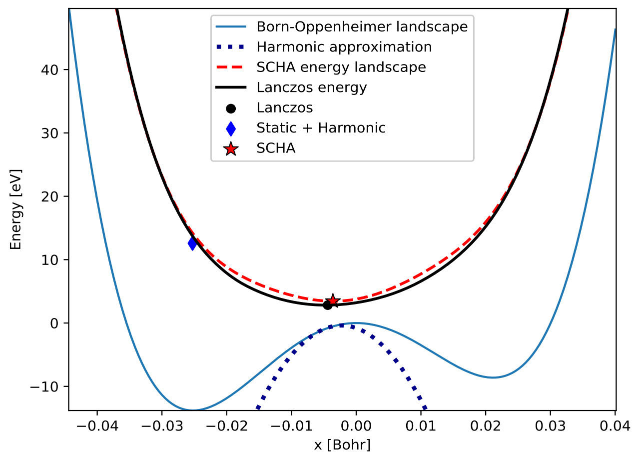


Structure stability

$$E_s(\mathcal{R}) = \min_{\Upsilon} \mathrm{Tr}[\rho_S(\mathcal{R}, \Upsilon) H]$$

This is equivalent to study how the energy changes if we move the atoms using a static external electric field.



High-pressure Hydrogen

A long time challenge

- 1935: Metallic hydrogen was predicted to be stable over 25 GPa
- 1968: Metallic hydrogen is a superconductor $T_c > 300\,\mathrm{K}$
- 2015: Experimental realization of H_3S: $T_c = 203\,\mathrm{K}$

The highest T_c known

H_3S broke the record held by cuprates for 40 years (138 K)

A “bit” more difficult than expected

In 1935 Hungtington and Wigner were wrong:

25 GPa

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A “bit” more difficult than expected

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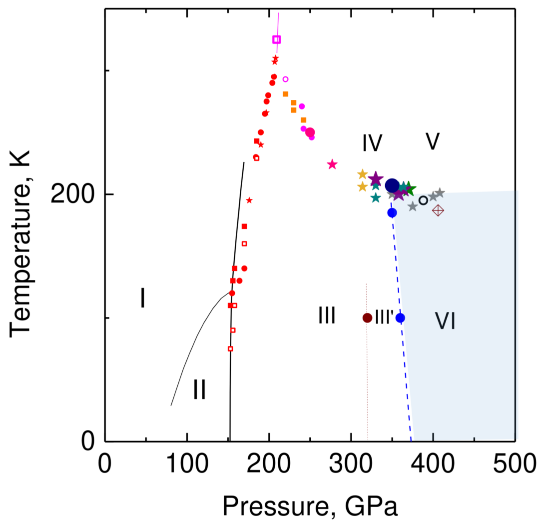
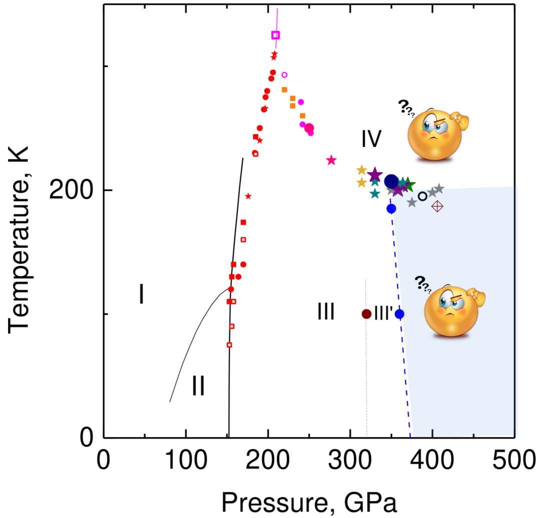
500 GPa

The high-pressure phase-diagram



[Eremets et al, Molecular semimetallic hydrogen, Arxiv, 2017]

The high-pressure phase-diagram



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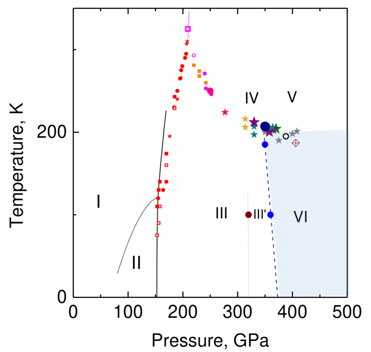
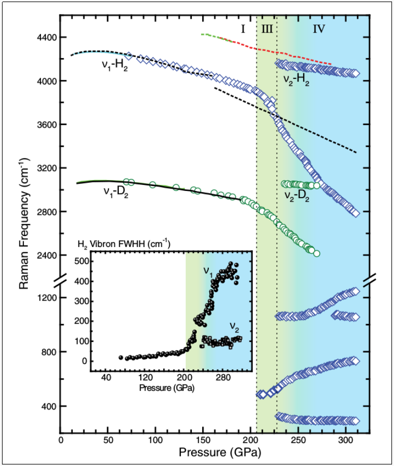
Vibrational spectroscopy is the only insight on the structure

The phase diagram:



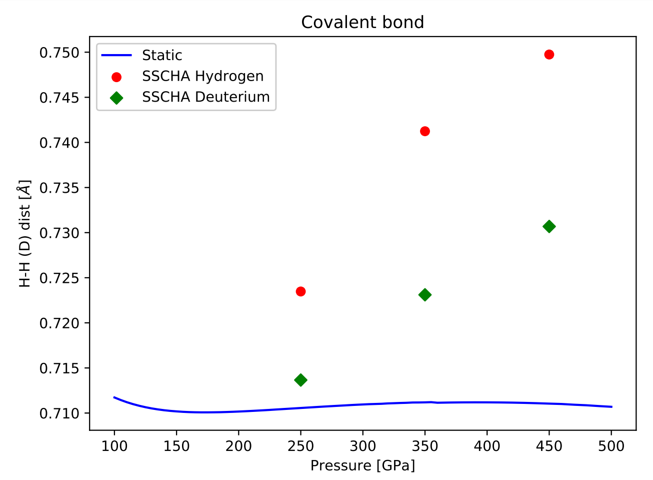


[Howie et al, Mixed Molecular and Atomic Phase of Dense Hydrogen, PRL, 2012]

SCHA and Hydrogen

Structure deformation

Anharmonicity and quantum zero-point motion stretches the H_2 molecules when increasing the pressure:



Structure deformation

Anharmonic Stress Tensor

Anharmonicity wants to separate the parallel planes of layered structures

250 GPa

$$\begin{array}{cccc} & x & y & z \\ x & \mathbf{6.1} & 0 & 0 \\ y & 0 & \mathbf{12.2} & 0 \\ z & 0 & 0 & \mathbf{6.0} \end{array}$$

[GPa]

350 GPa

$$\begin{array}{cccc} & x & y & z \\ x & \mathbf{5.1} & 0 & 0 \\ y & 0 & \mathbf{15.7} & 0 \\ z & 0 & 0 & \mathbf{4.7} \end{array}$$

[GPa]

450 GPa

$$\begin{array}{cccc} & x & y & z \\ x & \mathbf{5.1} & 0 & 0 \\ y & 0 & \mathbf{18.3} & 0 \\ z & 0 & 0 & \mathbf{4.1} \end{array}$$

[GPa]

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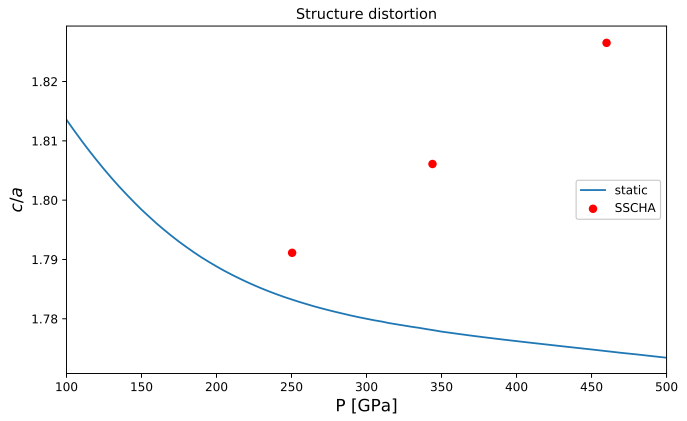
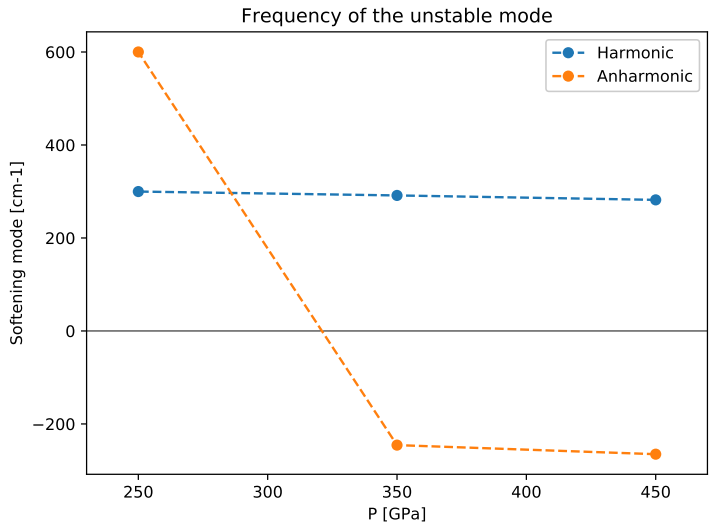


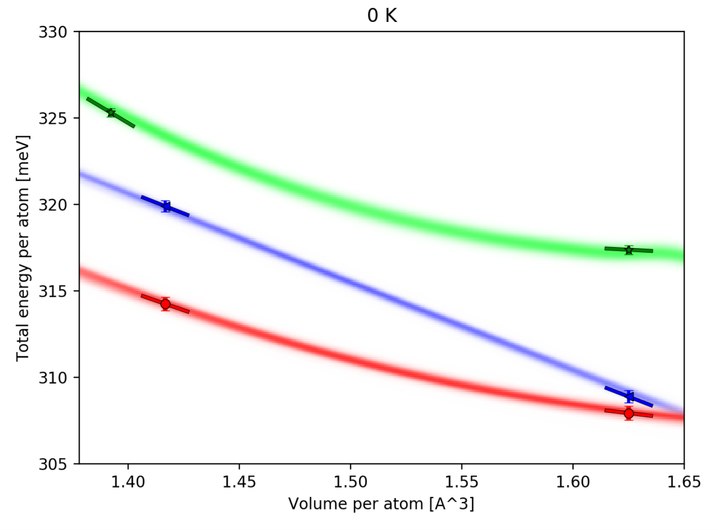
Stability of the structure

Unexpected Phase transition when increasing pressure.



SCHA get the full phase-diagram

We can get the phase-diagram with few calculations!



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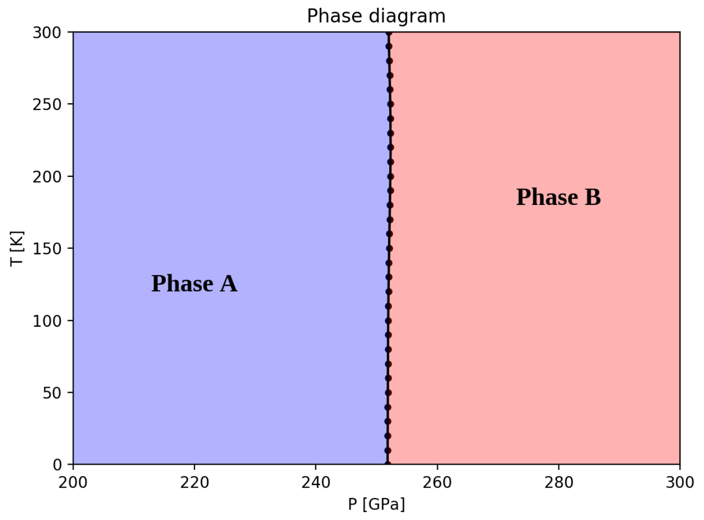

Conclusions

Within the SCHA we can do:

- Structure relaxation
- Structure stability
- Phase diagram